PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 5 : A01N 37/16

A1

(11) International Publication Number: WO 94/23575

(43) International Publication Date: 27 October 1994 (27.10.94)

(21) International Application Number: PCT/US94/02134

(22) International Filing Date: 24 February 1994 (24.02.94)

(30) Priority Data:
08/047, 264 12 April 1993 (12.04.93) US

(71) Applicant: ECOLAB INC. [US/US]; Ecolab Center, St. Paul, MN 55102 (US).

(72) Inventors: OAKES, Thomas, R.; 7816 Demontreville Trail N., Lake Elmo, MN 55042 (US). BOUFFORD, Thomas, G.; 934 Waterford Drive E., Eagan, MN 55123 (US).

(74) Agent: MAU, Michael, L.; Merchant, Gould, Smith, Edell, Welter & Schmidt, 1000 Norwest Center, 55 East Fifth Street, St. Paul, MN 55101 (US).

(81) Designated States: AU, CA, CN, JP, NZ, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).

Published
With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: PEROXYACID ANTIMICROBIAL COMPOSITION

(57) Abstract

A peroxyacid antimicrobial concentrate and use composition is provided comprising a C_5 peroxyacid in combination with a C_1-C_4 peroxyacid, a C_6-C_{18} peroxyacid, or mixtures thereof. The combination of these peracids produces a synergistic effect, providing a much more potent biocide than can be obtained by using these components separately. Other components can be added to the composition such as hydrotrope coupling agents, stabilizers, etc. An effective antimicrobial use solution is formed at low concentrations when the concentrate composition is diluted with water. Sanitizing of substantially fixed, "in-place" processing lines in dairies, breweries, and other food processing operations is one utility of the composition.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgystan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo			SE	Sweden
CH	Switzerland	KR	Republic of Korea	SI	Slovenia
CI	Côte d'Ivoire	KZ	Kazakhstan	SK	Slovakia
CM	Cameroon	LI	Liechtenstein	SN	Senegal
CN	China	LK	Sri Lanka	TD	Chad
CS	Czechoslovakia	LU	Luxembourg	TG	Togo
CZ	Czech Republic	LV	Latvia	TJ	Tajikistan
DE	Germany	MC	Monaco	TT	Trinidad and Tobago
DK	Denmark	MD	Republic of Moldova	UA	Ukraine
ES	Spain	MG	Madagascar	US	United States of America
FI	Finland	ML	Mali	UZ	Uzbekistan
FR	France	MN	Mongolia	VN	Viet Nam
GA	Gabon				

PEROXYACID ANTIMICROBIAL COMPOSITION

Field of the Invention

The invention relates generally to antimicrobial or biocidal compositions. More particularly, the invention relates to peroxyacid antimicrobial concentrates and use solutions which can sanitize surfaces, facilities and equipment found in food manufacture and food processing and food service industries, and typically hard non-porous surfaces in the health care industry.

Background of the Invention

Antimicrobial compositions are particularly needed in the food and beverage industries to clean and sanitize processing facilities such as pipelines, tanks, mixers, etc. and continuously operating homogenation or pasteurization apparatus. Sanitizing compositions have been formulated in the past to combat microbial growth in such facilities. For example, Wang, U.S. Patent No. 4,404,040, teaches a short chain fatty acid sanitizing composition comprising an aliphatic short chain fatty acid, a hydrotrope solubilizer capable of solubilizing the fatty acid in both the concentrate and use solution, and a hydrotrope compatible acid so that the use solution has a pH in the range of 2.0 to 5.0.

Peroxy-containing compositions are known for use in the production of microbicidal agents. One such composition is disclosed in Bowing et al., U.S. Patent No. 4,051,059 containing peracetic acid, acetic acid or mixtures of peracetic and acetic acid, hydrogen peroxide, anionic surface active compounds such as sulfonates and sulfates, and water.

Peracetic acid, generally using some concentrations of acetic acid and hydrogen peroxide has been shown to be a good biocide, but only at fairly high concentrations (generally greater than 100 parts peracetic acid per million (ppm)). Similarly, peroxyfatty acids have also been shown to be biocidal,

but only at high concentrations (greater than 200 ppm), such as in the composition disclosed in European Patent Application No. 233,731. Peroxyacetic acid is a good biocide, but it possesses a very strong odor, especially in the concentrate. For general use applications, for example, as a floor disinfectant or as an automatic dish wash destainer or sanitizer, it is desirable to have a product with low odor. Thus, it is desirable to obtain a low odor peroxy antimicrobial formulation that is at least as effective as peroxyacetic acid.

Antimicrobial compositions having low use concentrations (less than 100 ppm) which effectively kill microbes are particularly desirable. Low concentrations minimize use cost, surface corrosion, odor, carryover of biocide into foods and potential toxic effects to the user. Therefore, a continuing need exists to provide such an antimicrobial composition for use in food processing, food service and health care facilities. In contrast to the prior art, the composition of the present invention has the unique advantage of having unanticipated excellent antimicrobial or biocidal activity at low level use concentrations.

Summary of the Invention

The invention includes a peroxyacid antimicrobial concentrate and diluted end use composition comprising an effective biocidal amount of either a C_1-C_4 peroxyacid, and an effective biocidal amount of a C_6-C_{18} peroxyacid. The invention also includes a concentrate composition comprising the combination of an effective biocidal amount of a C_5 peroxyacid with an effective biocidal amount of a C_1-C_4 peroxyacid or a C_6-C_{18} peroxyacid. All three components of a C_1-C_4 peroxyacid, C_5 peroxyacid, and C_6-C_{18} peroxyacid can also be combined in the composition of the invention.

The above concentrate compositions can be diluted with a major proportion of water to form antimicrobial sanitizing use solutions having a pH in the range of about 2 to 8. When a C_1-C_4 peroxyacid is used, its concentration is at least about 10 ppm, preferably about 10 to 75 ppm. When a C_5 peroxyacid is used, its concentration is at least about 10 ppm, preferably about 20 to 100 ppm. When a C_6-C_{18} peroxyacid is used, its concentration is at least about 1 ppm, preferably about 1 to 25 ppm. Other components may be added such as a hydrotrope coupling agent for solubilizing the peroxyfatty acid in the concentrate form and when the concentrate composition is diluted with water.

In contrast to the prior art, we have discovered that at a low pH (e.g. preferably less than 5), C_6-C_{18} peroxyacids such as peroxyfatty acids are potent biocides at low levels. When used in combination with a C_1-C_4 peroxyacid such as peroxyacetic acid or a C_5 peroxyacid such as peroxyglutaric acid, a synergistic effect is obtained, providing a much more potent biocide than can be obtained by using these components separately. This means that substantially lower concentrations of biocide can be used to obtain equal cidal effects, leading to lower costs of the product and less potential for corrosion.

For example, we now have shown that combinations of peroxyglutaric acid and peroxyoctanoic acid possess surprisingly good bacterial kill properties at low concentrations, and both the use solution and concentrated composition possess low odor. This composition can be made by adding a mixture of glutaric acid and octanoic acid to a solution of hydrogen peroxide in the presence of a stabilizer and a solubilizer. We have demonstrated, using ^{13}C NMR spectroscopy, that both peroxyacids form in the above mixtures. That is, by merely adding the parent carboxylic acids to a properly stabilized hydrogen

peroxide system, the peroxyacids can be formed in sufficient quantity to give good bacterial kill at relatively low concentrations (e.g., about 50 ppm total peroxyacids by titration). From antimicrobial testing, we know that mixtures of peroxyglutaric acid and peroxyoctanoic acid are surprisingly effective, and that only small amounts of peroxyoctanoic acid are needed to greatly enhance the activity of a peroxyglutaric acid formula. The resulting activity is greater than the arithematic sum of the activity of each material separately.

As the term is used herein, a C_6-C_{18} peroxyacid (or peracid) is intended to mean the product of the oxidation of a C_6-C_{18} acid such as a fatty acid, or a mixture of acids, to form a peroxyacid or mixture of oxidized acids having from about 6 to 18 carbon atoms per molecule. The term C_1-C_4 peroxyacid is intended to mean the product of the oxidation of a C_1-C_4 carboxylic acid, or a mixture of acids thereof resulting in a single C_{1-4} peroxyacids or a mixture of such peroxyacids. This includes both simple and substituted C_1-C_4 carboxylic acids. The term C_5 peroxyacid is intended to mean the product of the oxidation of a C_5 carboxylic acid.

A method of sanitizing a surface, facilities or equipment comprises the steps of contacting the surface, facilities or equipment with the use solution made from the above concentrate compositions of the invention at a temperature in the range of about 4°C to 60°C. The composition is then circulated or left in contact with the facilities or equipment for a time sufficient to sanitize (generally at least 30 seconds) and the composition is thereafter drained or removed from the facilities or equipment.

One aspect of the invention are the novel, antimicrobial concentrate compositions which are capable of being diluted with a major proportion of water to

form sanitizing use solutions. A further aspect of the invention is the aqueous antimicrobial sanitizing use solutions which are particularly suited for "in-place" cleaning applications. Another aspect of the invention is a method of employing the use solutions in the cleaning or sanitizing of various process facilities or equipment as well as other surfaces.

Detailed Description of the Invention

The invention resides in peroxyacid antimicrobial concentrate and use compositions comprising various combinations of a C_5 peroxyacid, with a C_1-C_4 peroxyacid, or a C_6-C_{18} peroxyacid. We have found that combining these acids produces an antimicrobial effect that is greater than the arithmatic sum of the activity of the individual acids, antimicrobial activity, producing a much more potent biocide than can be obtained by using these components separately. The concentrate compositions can be diluted with a major proportion of water to form antimicrobial sanitizing use solutions having a pH in the range of about 2 to 8. The sanitizing use solutions can be used effectively to clean or sanitize facilities and equipment used in the food processing, food service and health care industries.

Peracids

The present invention is based upon the surprising discovery that when a C_5 peroxy acid is combined with a C_6-C_{18} peroxyacid or a C_1-C_4 peroxyacid, a synergistic effect is produced and greatly enhanced antimicrobial activity is exhibited when compared to the C_5 peroxyacid, the C_6-C_{18} peroxyacid or the C_1-C_4 peroxyacid alone. The present composition blends can effectively kill microorganisms (e.g., a 5 $\log_{10}$ reduction in 30 seconds) at a concentration level below 100 ppm and as low as 20 ppm of the peracid blend.

The preferred C_5 peroxyacid for use in the present invention is peroxyglutaric acid which is made from glutaric acid having the formula $CO_3H(CH_2)_3CO_3H$. The peroxyglutaric acid can be monoperoxy, diperoxy or mixtures of monoperoxy and diperoxy acids. Aqueous solutions of peroxyglutaric acid containing an excess of hydrogen peroxide (H_2O_2) and, if appropriate, also a stabilizer known for H_2O_2 can be employed in the invention. Such solutions contain about 1 to 60 wt-% of peroxyglutaric acid, about 1 to 50 wt-% of H_2O_2, about 0 to 50 wt-% of glutaric acid, and the remainder water. About 0.01 to 2 wt-% of a stabilizer can be used such as urea or 2,3-pyridinedicarboxylic acid and/or 2,6-pyridinedicarboxylic acid. We have found that these peroxyglutaric acid materials have surprising solubility in aqueous systems and low odor.

A variety of C_6-C_{18} peroxyacids may be employed in the composition of the invention such as peroxyfatty acids, monoperoxy- or diperoxydicarboxylic acids, and peroxy aromatic acids. The C_6-C_{18} peroxyacids employed in the present invention may be structurally represented as follows: R_1-CO_3H, wherein R_1 is a hydrocarbon moiety having from about 5 to 17 carbon atoms (a C_8 peroxyacid is generally represented structurally as C_7-CO_3H). R_1 may have substituents in the chain, e.g., -OH, CO_2H, or heteroatoms (e.g., -O- as in alkylether carboxylic acids), as long as the antimicrobial properties of the overall composition are not significantly affected. The "R_1" substituents or heteroatoms may change the overall acidity (i.e., pKa) of the carboxylic acids herein described. Such modification is within the contemplation of the present invention provided the advantageous antimicrobial performance is maintained. Furthermore, R_1 may be linear, branched, cyclic or aromatic. Preferred hydrocarbon moieties (i.e. preferred R_1's) include linear, saturated, hydrocarbon

aliphatic moieties having from 7 to 11 carbon atoms (or 8 to 12 carbon atoms per molecule).

Specific examples of suitable C_6-C_{18} carboxylic fatty acids which can be reacted with hydrogen peroxide to form peroxyfatty acids include such saturated fatty acids as hexanoic (C_6), enanthic (heptanoic) (C_7), caprylic (octanoic) (C_8), perlargonic (nonanoic) (C_9), capric (decanoic) (C_{10}), undecyclic (undecanoic) (C_{11}), lauric (dodecanoic) (C_{12}), trideclic (tridecanoic) (C_{13}), myristic (tetradecanoic) (C_{14}), palmitic (hexadecanoic) (C_{16}), and stearic (octodecanoic) (C_{18}). These acids can be derived from both natural and synthetic sources. Natural sources include animal and vegetable fats or oils which should be fully hydrogenated. Synthetic acids can be produced by the oxidation of petroleum wax. Particularly preferred peroxyfatty acids for use in the composition of the invention are linear monoperoxy aliphatic fatty acids such as peroxyoctanoic acid, peroxydecanoic acid, or mixtures thereof.

Other suitable C_6-C_{18} peroxyacids are derived from the oxidation of dicarboxylic acids and aromatic acids. Suitable dicarboxylic acids include adipic acid (C_6) and sebacic acid (C_{10}). Examples of a suitable aromatic acid include benzoic acid, phthalic acid, terephthalic acid, hydroxy benzoic acid, etc. These acids can be reacted with hydrogen peroxide to form the peracid form suitable for use in the composition of the invention. Preferred peracids in this group include monoperoxy- or diperoxyadipic acid, monoperoxy- or diperoxysebacic acid, and peroxybenzoic acid.

The C_1-C_4 peroxyacid component can be derived from a C_1-C_4 carboxylic acid or dicarboxylic acid by reacting the acid with hydrogen peroxide. Examples of suitable C_1-C_4 carboxylic acids include acetic acid, propionic acid, glycolic acid, and succinic acid. Preferable C_1-C_4 peroxycarboxylic acids for use in the composition of the invention include peroxyacetic acid, peroxypropionic

acid, peroxyglycolic acid, peroxysuccinic acid, or mixtures thereof.

The above peroxyacids provide antibacterial activity against a wide variety of microorganisms, such as gram positive (e.g., Staphylococcus aureus) and gram negative (e.g., Escherichia coli) microorganisms, yeast, molds, bacterial spores, etc. When combined, the above peroxyacids have greatly enhanced activity compared to a C_1-C_4 peroxyacid, a C_5 peroxyacid, or a C_6-C_{18} peroxyacid alone.

The antimicrobial concentrates of the present invention can comprise about 0 to 10 wt-%, preferably about 0.05 to 5 wt-%, and most preferably about 0.1 to 2 wt-% of a C_6-C_{18} peroxyacid; about 0 to 30 wt-%, preferably about 1 to 25 wt-%, and most preferably about 5 to 20 wt-% of a C_5 peroxyacid; and about 0 to 25 wt-%, preferably about 0.5 to 20 wt-%, and most preferably about 1 to 15 wt-% of a C_1-C_4 peroxyacid. One concentrate composition preferably has a weight ratio of C_1-C_4 peroxyacid to C_6-C_{18} peroxyacid of about 15:1 to 3:1. Another concentrate composition preferably has a weight ratio of C_5 peroxyacid to C_6-C_{18} peroxyacid of about 20:1 to 2:1. A further concentrate composition has a weight ratio of C_5 peroxyacid to C_1-C_4 peroxyacid of about 10:1 to 1:10. The concentrate compositions contain sufficient acid so that the end use solution has a pH of about 2 to 8, preferably about 3 to 7. Some acidity may come from an inert acidulant which may be optionally added (e.g., phosphoric acid).

The peracid components used in the composition of the invention can be produced in a simple manner by mixing a hydrogen peroxide (H_2O_2) solution with the desired amount of carboxylic acid or acid blend. With the higher molecular weight fatty acids, a hydrotrope coupler may be required to fully solubilize the fatty acid. The H_2O_2 solution also can be added to previously made peroxyacids such as peroxyacetic acid,

peroxyglutaric acid or various peroxy fatty acids to produce the peroxyacid composition of the invention. The concentrates can contain about 1 to 50 wt-%, preferably about 5 to 25 wt-% of hydrogen peroxide.

The concentrate compositions can further comprise a free C_6-C_{18} carboxylic acid, a free C_5 carboxylic acid, a free C_1-C_4 carboxylic acid, or mixtures thereof. The free acids will preferably correspond to the starting materials used in the preparation of the peroxyacid components. The free C_6-C_{18} carboxylic acid is preferably linear and saturated, has 8 to 12 carbon atoms per molecule, and can also comprise a mixture of acids. The free C_6-C_{18} carboxylic acid, free C_5 carboxylic acid, and free C_1-C_4 carboxylic acid can be present as a result of an equilibrium reaction with the hydrogen peroxide to form the peroxyacids.

Optional Components

Various optional materials may be added to the composition of the invention to help solubilize the fatty acids, restrict or enhance the formation of foam, to control hard water, to stabilize the composition, or to further enhance the antimicrobial activity of the composition.

The compositions of the invention can contain a surfactant hydrotrope coupling agent or solubilizer that permits blending both fatty acids and short chain perfatty acids in aqueous liquids. Functionally speaking, the suitable couplers which can be employed are non-toxic and retain the fatty acid and the perfatty acid in aqueous solution throughout the temperature range and concentration to which a concentrate or any use solution is exposed.

Any hydrotrope coupler may be used provided it does not react with the other components of the composition or negatively affect the antimicrobial properties of the composition. Representative classes of hydrotropic

coupling agents or solubilizers which can be employed include anionic surfactants such as alkyl sulfates and alkane sulfonates, linear alkyl benzene or naphthalene sulfonates, secondary alkane sulfonates, alkyl ether sulfates or sulfonates, alkyl phosphates or phosphonates, dialkyl sulfosuccinic acid esters, sugar esters (e.g., sorbitan esters) and C_8-C_{10} alkyl glucosides. Preferred coupling agents for use in the present invention include n-octanesulfonate, available as NAS 8D from Ecolab, and the commonly available aromatic sulfonates such as the alkyl benzene sulfonates (e.g. xylene sulfonates) or naphthalene sulfonates.

Some of the above hydrotropic coupling agents independently exhibit antimicrobial activity at low pH. This adds to the efficacy of the present invention, but is not the primary criterion used in selecting an appropriate coupling agent. Since it is the presence of perfatty acid in the protonated neutral state which provides biocidal activity, the coupling agent should be selected not for its independent antimicrobial activity but for its ability to provide effective interaction between the substantially insoluble perfatty acids described herein and the microorganisms which the present compositions control.

The hydrotrope coupling agent can comprise about 0.1 to 30 wt-%, preferably about 1 to 20 wt-%, and most preferably about 2 to 15 wt-% of the concentrate composition.

Compounds such as mono, di and trialkyl phosphate esters may be added to the composition to suppress foam. Such phosphate esters would generally be produced from aliphatic linear alcohols, there being from 8 to 12 carbon atoms in the aliphatic portions of the alkyl phosphate esters. Alkyl phosphate esters possess some antimicrobial activity in their own right under the conditions of the present invention. This antimicrobial activity also tends to add to the overall antimicrobial

activity of the present compositions even though the phosphate esters may be added for other reasons. Furthermore, the addition of nonionic surfactants would tend to reduce foam formation herein. Such materials tend to enhance performance of the other components of the composition, particularly in cold or soft water. A particularly useful nonionic surfactant for use as a defoamer is nonylphenol having an average of 12 moles of ethylene oxide condensed thereon, it being encapped with a hydrophobic portion comprising an average of 30 moles of propylene oxide.

A variety of chelating agents can be added to the composition of the invention to enhance biological activity, cleaning performance and stability of the peroxyacids. For example, 1-hydroxyethylidene-1,1-diphosphonic acid commercially available from the Monsanto Company under the designation "DEQUEST 2010" has been found to be effective. Other effective chelating agents include 1,6 pyridine dicarboxylic acid. Chelating agents can be added to the present composition to control or sequester hardness ions such as calcium and magnesium. In this manner both detergency and sanitization capability can be enhanced.

Other materials which are sufficiently stable at the low pH contemplated by the present composition may be added to the composition to impart desirable qualities depending upon the intended ultimate use. For example, phosphoric acid (H_3PO_4) can be added to the composition of the invention. Additional compounds can be added to the concentrate (and thus ultimately to the use solution) to change its color or odor, to adjust its viscosity, to enhance its thermal (i.e., freeze-thaw) stability or to provide other qualities which tend to make it more marketable.

The compositions of the invention can be made by combining by simple mixing at least two of a C_6-C_{18} peroxyacid, a C_1-C_4 peroxyacid, and a C_5 peroxyacid.

These compositions could be formulated with preformed peroxyacids. A preferred composition of the invention can be made by mixing a C_5 carboxylic acid with a C_1-C_4 carboxylic acid or an aliphatic C_6-C_{18} carboxylic acid, optionally a coupler and/or a stabilizer, and reacting this mixture with hydrogen peroxide. A stable equilibrium mixture is produced containing a C_5 peroxyacid and a C_1-C_4 peroxyacid or an aliphatic C_6-C_{18} peroxyacid by allowing the mixture to stand for from one to seven days at 15°C to 25°C. As with any aqueous reaction of hydrogen peroxide with a free carboxylic acid, this gives a true equilibrium mixture. In this case, the equilibrium mixture will contain hydrogen peroxide, an unoxidized C_5 carboxylic acid, an unoxidized C_1-C_4 carboxylic acid or an unoxidized aliphatic C_6-C_{18} carboxylic acid, a C_5 peroxyacid, a C_1-C_4 peroxyacid or an aliphatic C_6-C_{18} peroxyacid, and optionally various couplers and/or stabilizers.

By using the above approach, the compositions of the invention can be formulated by merely mixing readily available raw materials, e.g., glutaric acid, acetic acid, hydrogen peroxide and fatty acid. By allowing solution time for equilibrium to be obtained, the product containing the active biocides is obtained. In varying the ratio of C_5 carboxylic acid to C_1-C_4 carboxylic acid or C_6-C_{18} carboxylic acid, it is easy to vary the ratio of C_5 peroxyacid to C_1-C_4 peroxycarboxylic acid or C_6-C_{18} peroxyacid.

Concentrate and Use Compositions

The present invention contemplates a concentrate composition which is diluted to a use solution prior to its utilization as a sanitizer. Primarily for reasons of economics, the concentrate would normally be marketed and the end user would dilute the concentrate with water to a use solution. Preferred antimicrobial concentrate compositions comprise about 1 to 25 wt-%, preferably

about 5 to 20 wt-%, of a C_5 peroxyacid, about 0.01 to 10 wt-%, preferably about 0.05 to 5 wt-%, of a C_6-C_{18} peroxyfatty acid, and/or about 0.1 to 25 wt-%, preferably about 0.5 to 20 wt-%, of a C_1-C_4 peroxyacid. The concentrate compositions can further include about 0.1 to 30 wt-% of a hydrotrope coupling agent, and about 1 to 50 wt-% of hydrogen peroxide. Other acidulants may optionally be employed in the compositions such as phosphoric acid. All three of the above peroxyacids may be combined together in the above amounts to form an effective antimicrobial concentrate composition.

The level of active components in the concentrate composition is dependent upon the intended dilution factor and desired acidity in the use solution. The C_6-C_{18} peroxyacid component is generally obtained by reacting a C_6-C_{18} carboxylic acid with hydrogen peroxide in the presence of a C_1-C_4 carboxylic acid and/or a C_5 carboxylic acid. The resulting concentrate is diluted with water to provide the use solution. Generally, a dilution of 1 fluid oz. to 4 gallons (i.e. dilution of 1 to 500 by volume) or to 8 gallons (i.e. dilution of 1 to 1,000 by volume) of water can be obtained with 2% to 20% total peracids in the concentrate. Higher use dilution can be employed if elevated use temperature (greater than 20° C) or extended exposure time (greater than 30 seconds) are also employed.

In its intended end use, the concentrate is diluted with a major proportion of water and used for purposes of sanitization. The typical concentrate composition described above is diluted with available tap or service water to a formulation of approximately 1 oz. concentrate to 8 gallons of water. Aqueous antimicrobial sanitizing use solutions can comprise at least about 1 part per million (ppm), preferably about 10 to 100 ppm, of a C_5 peroxyacid, at least about 1 ppm, preferably about 2 to 10 ppm of a C_6-C_{18} peroxyacid, and/or at least about 10 ppm, preferably about 20 to 50

ppm of a C_1-C_4 peroxyacid. Any two of the above peracids may be present in the use solution or all three may be present, depending on the concentrate composition ingredients. In a preferred composition, the weight ratio of C_6-C_{18} peroxyacid to C_5 peroxyacid ranges from about 0.01 to 0.5 parts, preferably about 0.02 to 0.2 parts, of C_6-C_{18} peroxyacid per part of C_5 peroxyacid. Preferably the total peracid concentration in the use solution is less than about 75 ppm, and most preferably between about 5 to 50 ppm. Higher levels of peracids can be employed in the use solution to obtain disinfecting or sterilizing results.

The aqueous use solution can further comprise at least about 1 ppm, preferably about 2 to 20 ppm, of a hydrotrope coupling agent, and at least about 1 ppm, preferably about 2 to 200 ppm of hydrogen peroxide. The use solution can also comprise at least about 1 ppm, preferably about 2 to 200 ppm of a free C_6-C_{18} carboxylic acid, a free C_5 carboxylic acid, a free C_1-C_4 carboxylic acid, or mixtures thereof. The aqueous use solutions have a pH in the range of about 2 to 8, preferably about 3 to 7.

Methods of Use

As noted above, the present composition is useful in the cleaning or sanitizing of processing facilities or equipment in the food service, food processing or health care industries. Examples of process facilities in which the composition of the invention can be employed include a dairy, milk line, a continuous brewing system, food processing lines such as pumpable food systems and beverage lines, etc. Food service wares can also be sanitized with the composition of the invention. The composition is also useful in sanitizing or disinfecting solid surfaces such as floors, counters, furniture, medical tools and equipment, etc., found in the health care industry. Such surfaces often become contaminated

with liquid body spills such as blood, other hazardous body fluids or mixtures thereof.

Generally, the actual cleaning of the in-place system or other surface (i.e., removal of unwanted offal therein) is accomplished with a different material such as a formulated detergent which is introduced with heated water. After this cleaning step, the instant sanitizing composition would be applied or introduced into the system at a use solution concentration in unheated, ambient temperature water. The present sanitizing composition is found to remain in solution in cold (e.g., 40°F/4°C) water and heated (e.g., 140°F/60°C) water. Although it is not normally necessary to heat the aqueous use solution of the present composition, under some circumstances heating may be desirable to further enhance its antimicrobial activity.

A method of sanitizing substantially fixed in-place process facilities comprises the following steps. The use solution composition of the invention is introduced into the process facilities at a temperature in the range of about 4 to 60°C. After introduction, the use solution is circulated throughout the system for a time sufficient to sanitize the process facilities (i.e., to kill undesirable microorganisms). After the system has been sanitized by means of the use solution composition, the use solution is drained from the system. Upon completion of the sanitizing step, the system optionally may be rinsed with other materials such as potable water. The composition is preferably circulated through the process facilities for 10 minutes or less and allowed to drain without further treatment.

The composition may also be employed by dipping food processing equipment into the use solution, soaking the equipment for a time sufficient to sanitize the equipment, and draining excess solution off the equipment. The composition may be further employed by

spraying or wiping food processing surfaces with the use solution, keeping the surfaces wet for a time sufficient to sanitize the surfaces, and removing excess solution by draining vertically, vacuuming, etc.

The composition of the invention may also be used in a method of sanitizing hard surfaces such as institutional type equipment, utensils, dishes, health care equipment or tools, and other hard surfaces. The composition may also be employed in sanitizing clothing items or fabric which has become contaminated. The composition is contacted with any of the above contaminated surfaces or items at use temperatures in the range of about 4 to 60°C., for a period of time effective to sanitize, disinfect, or sterilize the surface or item. For example, the concentrate composition can be injected into the wash or rinse water of a laundry machine and contacted with contaminated fabric for a time sufficient to sanitize the fabric. Excess solution can then be removed by rinsing or centrifuging the fabric.

As the term "sanitizing" is used in the method of the instant invention, it means a reduction in the population numbers of undesirable microorganisms by about 5 powers of 10 or greater (i.e., at least 5 orders of magnitude) after a 30 second exposure time. It is to be emphasized that the instant use solution provides cleaning as well as sanitizing performance although its primary utility is sanitizing. The composition may also be used to achieve disinfection or sterilization (i.e., elimination of all microorganisms) by employing higher levels of peracids in the use solution.

The following Examples which contain a best mode, are intended to illustrate the above invention and should not be construed as to narrow its scope. One skilled in the art will readily recognize that these Examples suggest many other ways in which the present invention could be practiced. Examples 1-14 demonstrate

cooperation between C_{1-4} peracids and C_{6-18} peracids. Examples 15 and 16 demonstrate the superiority of a C_5 peracid in combination with either a C_{1-4} peracid, or a C_{6-18} peracid. Examples 17-32 demonstrate the efficacy of the blends preparative information, stability, and aging tests.

Example 1

Experiments were conducted to determine the antimicrobial efficacy of pure peroxyacids. Table I below demonstrates the antimicrobial efficacy of pure peroxyacids at very low levels when exposed to S. aureus and E. coli. The peroxyacids listed in Table I were tested by diluting them in 0.05 M citrate buffer made in distilled water and were exposed to the bacteria for 30 seconds at 20°C. As Table I indicates, the diperoxyacids were somewhat less active than the peroxyfatty acids. Peroxydecanoic acid was very effective at very low levels against S. aureus, but higher levels were required to be effective against E. coli. Higher levels were also required at pH 5.

TABLE I

Comparison of Cidal Activity of Peroxyacids

Peroxyacid	pH	Minimum concentration required for 5 log reduction (ppm)[a]	
		S. aureus	*E. coli*
Peroxyhexanoic (C_6)	3.5	15	15
	5.0	20	15
Diperoxyadipic (C_6)	3.5	>50	40
	5.0	>60	35
Peroxyoctanoic (C_8)	3.5	5	5
	5.0	10	15
Peroxydecanoic (C_{10})	3.5	3	10
	5.0	1	30
Diperoxysebacic (C_{10})	3.5	15	15
	5.0	10	50

[a] - Peroxyacids tested at 5-ppm increments, or at 1, 3, and 5 ppm where appropriate.

In Table II below, the degree of antimicrobial kill resulting from a cooperation between the C_2 and C_3 peroxyacids when combined with C_8 and C_{10} peroxyfatty acids is shown. As Table II shows, there was little or no antimicrobial activity when the C_2 and C_3 peroxyacids and the C_8 and C_{10} peroxyfatty acids were tested alone. However, when a C_2 or C_3 peroxyacid was combined with a C_8 or C_{10} peroxyfatty acid, the bacterial kill of E. coli surprisingly increased. These tests were conducted at pH 4.5 or 5 (see Table II).

TABLE II

Cooperative Interaction of Peroxyacids

C_2 [Peroxyacetic] (ppm)	C_3 [Peroxypropionic] (ppm)	C_8 [Peroxyoctanoic] (ppm)	C_{10} [Peroxydecanoic] reduction (ppm)	Microbial Population Log Reduc.
25		0		0[a]
0		5		0.1[a]
25		5		3.8[a]
	25	0		0.3[b]
	0	6		0.1[b]
	25	6		3.9[b]
30			0	0.7[a]
0			6	0[a]
30			6	2.6[a]

[a] E. coli, pH 5, distilled water
[b] E. coli, pH 4.5, 500 ppm hard water

Examples 2-6

A two-component system containing peracetic acid and perfatty acid was formulated and tested to determine its sanitizing activity over just a peracetic acid system. Table III shows premixes 1 and 2 used in making the composition. The premixes were both made with H_2O_2 (35% solution), acetic acid, Dequest 2010, and with/without H_3PO4. Premix 1 was made about 5 months before premix 2. To each premix was added NAS 8D, a C_8 fatty acid or Emery 658 as shown in Table IV to complete the formulation of Examples 2-5. Example 6 was formulated as a control and had no fatty acid.

TABLE III

Peracid Premixes

	Wt-% Component	
Component	Premix 1	Premix 2
H_2O_2 (35%)	75.0	35.0
Acetic acid (glacial)	24.0	35.0
Dequest 2010	1.0	1.0
H_3PO_4 (85%)	--	29.0

TABLE IV

Perfatty Acid/Peracetic Acid Formulations

	Wt-% Ingredient				
Ingredient	Ex. 2	Ex.3	Ex.4	Ex.5	Ex.6
Premix 1	80.0	--	80.0	--	--
Premix 2	--	80.0	--	80.0	--
NAS 8D	10.0	10.0	10.0	10.0	--
C_8 Fatty Acid	10.0	10.0	--	--	--
Emery 658	--	--	10.0	10.0	--
Acetic Acid (Glacial)	--	--	--	--	24.0
H_2O_2 (35%)	--	--	--	--	75.0
Dequest 2010	--	--	--	--	1.0

Table V shows the sanitizing activity measured from each formulation of Examples 2-5 at 50, 100, or 150 ppm peracetic acid against S. aureus (Example 6 is a control).

TABLE V

Sanitizing Efficacy of Perfatty Acid/ Peracetic Acid System vs. Sanitizing Efficacy of Peracetic Acid System

Example	Total Peracid[a] (Percent)	Fatty Acid (Percent)	Test Concentration[a] (ppm)	Test pH	Log[b] Reduction
2	7.69	10.0	150	3.53	>7.06
			100	3.64	>7.06
			50	3.83	>7.06
3	11.21	10.0	150	2.71	>7.06
			100	2.80	>7.06
			50	3.08	>7.06
4	9.08	10.0	150	3.64	>7.06
			100	3.65	>7.06
			50	3.85	>7.06
5	10.92	10.0	150	2.68	>7.06
			100	2.77	>7.06
			50	3.10	>7.06
6	10.40	--	150	3.56	>7.06
			100	3.68	3.89
			50	3.93	NMA[c]

(a) As peracetic acid

(b) Average of duplicate testing against S. aureus.

(c) No measurable activity.

Extremely good kill (>7 log reduction) was obtained with or without H_3PO_4 in the perfatty acid formulations of Examples 2-6. The two component system of C_8 fatty acid or Emery 658 in combination with peracetic acid (Example 2-5) had significantly better kill than the peracetic acid system alone (Example 6) at a test concentration of 50 to 100 ppm. No activity was measured at 50 ppm with the single peracetic acid system of Example 6.

Example 7-10

The effect of alkyl chain length on antimicrobial efficacy of perfatty acids was determined for percaprylic (C_8) acid, percapric (C_{10}) acid and a percaprylic/percapric (3:1) perfatty acid mixture using the compositions of Examples 7-8 summarized in Table VI below.

TABLE VI

	Wt-% of Ingredient			
Ingredient	Ex.7	Ex.8	Ex.9	Ex.10
Percaprylic (C_8) Acid	1	--	--	--
Percapric (C_{10}) Acid	--	1	--	--
C_8 + C_{10} (3:1) Perfatty Acid	--	--	1	--
Acetic Acid	10	10	10	10
Water	84	84	84	85
NAS 8D	5	5	5	5

The antimicrobial efficacy of Examples 7-10 are summarized in Table VII below. Examples 7-9 were tested using three samples (a, b, c) of 5, 10, and 15 ppm of perfatty acid respectively. Example 10, containing no perfatty acid, was diluted to an equivalent formulation of

Examples 7-9 containing perfatty acid. As can be seen from Table VII, significant kill occurred at 5 ppm for S. aureus using Examples 7-9. Significant kill occurred against E. coli at 10 ppm of perfatty acid in Examples 7-9. Example 10 (having no perfatty acid) did not produce any kill of either microorganism.

TABLE VII

Antimicrobial Efficacy of Examples 7-10

Example	Sample	Perfatty Acid Concentration (ppm)	Log Kill S. aureus	Log Kill E. coli
7	a	5	>7.0	3.6
	b	10	--	>7.2
	c	15	--	>7.2
8	a	5	>7.0	3.0
	b	10	--	>7.2
	c	15	--	>7.2
9	a	5	>7.0	<3.0
	b	10	--	>7.2, 5.5
	c	15	--	>7.2
10	a	---[a]	0	--
	b	---[b]	--	0

[a] - Equivalent total product concentration as Examples 7, 8, 9 at 5 ppm perfatty acid.

[b] - Equivalent total product concentration as Examples 7, 8, 9 at 15 ppm perfatty acid.

Example 11

The antimicrobial activity of percaprylic acid against E. coli was measured at a 30 second exposure at varying pH's. The formulation contained 94% water, 5% NAS 8D, and 1% percaprylic acid. The formulation was diluted in a buffer of 0.05 M citrate and 0.05 M potassium phosphate. The log kill of this formulation at increasing pH's is summarized in Table VIII. Samples containing 7 ppm and 25

ppm of percaprylic acid were tested. As Table VIII indicates, significant kill at 7 ppm occurred at a pH of 3.0. Significant kill levels were maintained at 25 ppm through a pH of 7.0.

TABLE VIII

Antimicrobial Efficacy of Percaprylic Acid against E. coli

pH	Log Kill (Perfatty Concentration 7 ppm)	Log Kill (Perfatty Concentration 25 ppm)
3.0	>7.2	>7.2
5.0	<3.0	>7.2
7.0	<3.0	>7.2
8.9	--	<3.0
9.0	<3.0	--

Examples 12-14

The compositions of Examples 12-14 were made to determine the limitations on cidal activity of compositions containing at least 30% acetic acid. Higher acetic acid formulations were also tested for their cidal activity. The composition of Example 14 was prepared with no coupler (NAS 8D). The compositional ingredients of Examples 12-14 are summarized below in Table IX.

TABLE IX

	Wt-% of Ingredient		
Ingredient	Example 12	Example 13	Example 14
Acetic Acid	30.0	50.0	50.0
H_2O_2 (35%)	30.0	15.0	15.0
Dequest 2010	1.0	1.0	1.0
C_8 Fatty Acid	4.0	6.0	5.0
NAS 8D (Spray Dried)	5.0	5.0	--
Distilled Water	30.0	23.0	29.0

The antimicrobial efficacy of Examples 12-14 was determined using the procedure of the standard A.O.A.C. sanitizing test. The compositions of Examples 12-14 were diluted with 500 ppm hard water and employed at 25°C. The bacteria used in the test procedure were S. aureus and E. coli, and TGE plating medium was employed. Exposure time of the compositions to the bacteria was 30 seconds. The neutralizer employed in the testing procedure contained 0.1% thiosulfate, 1.0% peptone, and 0.025% catalase. The antimicrobial activity of Examples 12-14 is summarized in Table X below.

TABLE X

Cidal Activity of Examples 12-14

			Log Reduction	
Formulation	Concentration	pH	S. aureus	E. coli
Example 12	1 oz:8 gal.[a]	4.48	>7.15	>6.89
	1 oz:10 gal.[b]	4.83	>7.15	>6.89
	1 oz:12 gal.[c]	5.04	>7.15	6.41
	1 oz:14 gal.[d]	5.52	>7.15	5.76
	1 oz:16 gal.[e]	5.94	>7.15	2.95
Example 13	40 ppm Active	4.16	>7.15	>6.89
Example 14	40 ppm Active	4.04	>7.15	>6.89

[a] 54.2 ppm peracid
[b] 43.3 ppm peracid
[c] 36.1 ppm peracid
[d] 31.0 ppm peracid
[e] 27.2 ppm peracid

As Table X indicates, very low concentrations of combinations of peroxyacetic acid and peroxyfatty acid are very effective in killing bacteria. Also, Example 14 showed that the composition of the invention is antimicrobially effective without a hydrotrope coupler.

Example 15

Samples 1-10 were prepared to test the cidal activity of C_2, C_5, and C_8 peroxyacids, both alone and in various combinations. The peroxyacetic (C_2) acid was a production sample made by Ecolab Inc. under the trade name of Oxonia P3. Iodometric and ceric sulfate titrations on the day of microbiological testing gave a peroxyacetic acid concentration of 6.04%. The peroxyglutaric (C_5) acid was prepared by mixing 84 g of 35% hydrogen peroxide with 1 g of Dequest 2010 (Monsanto Corporation) and 15 g of glutaric acid. After standing for one week, the concentration of peroxyglutaric acid (by titration) had reached equilibrium. Titration on the day of microbiological testing gave a peroxyglutaric acid concentration of 11.42%. The peroxyoctanoic (C_8) acid was prepared by the method of W.E. Parker, C. Ricciuti, C.L. Ogg and D. Swern, J. Am. Chem. Soc. 77 4037 (1955), incorporated herein by reference. Several recrystalizations from low boiling petroleum ether gave the pure peroxyoctanoic acid. Titration on the day of microbiological testing showed the crystalline peroxyoctanoic acid to be 98-100% pure.

Microbiological test sample solutions were then made from each of the above peroxyacids. The Oxonia P3 (6.04% peroxyacetic acid) was first diluted 1:10 to obtain a working solution containing 6040 ppm of peroxyacetic acid. To obtain a 25 ppm use solution, 1.035 ml of this working solution was diluted to 250 ml with deionized water. To obtain a 50 ppm use solution, 2.07 ml of the working solution was similarly diluted to 250 ml. The peroxyglutaric acid (11.42% titratable peroxyglutaric acid) was diluted 1:20 with deionized water to obtain a 5710 ppm working solution of peroxyglutaric acid. To obtain a 25 ppm and a 50 ppm use solution, 1.095 ml and 2.189 ml were each diluted to 250 ml with deionized water. A solution of peroxyoctanoic acid was prepared by mixing 9.4144 g of

deionized water with 0.5021 g of sodium octane sulfonate (a non-active coupler) and 0.1017 g of pure peroxyoctanoic acid. A 1:10 dilution with deionized water gave a 1000 ppm working solution of peroxyoctanoic acid. A 5 ppm use solution of peroxyoctanoic acid was obtained by diluting 1.25 ml of the working solution to 250 ml with deionized water.

Mixtures of the various peroxyacids were prepared in a similar fashion by adding the appropriate amount of each peroxyacid working solution to a volumetric flask and diluting to 250 ml with deionized water. In all cases, the sample solutions were tested soon after dilution to assure that no decomposition of the peroxyacids had occurred.

The microbiological testing followed the standard AOAC procedure, AOAC Official Methods of Analysis, 15th Edition, 1990, Germicidal and Detergent Sanitizing Action of Disinfectants, with the addition of McIlvaine's citric acid-phosphate buffer to maintain the pH of the sanitizer solution at pH 4.5. Contact time was 30 seconds. Testing was done in duplicate with the following results as summarized in Table XI.

TABLE XI

COOPERATIVE INTERACTION OF PEROXYACIDS

Sample	C_2 (POAA[1])	C_5 (POGA[2])	C_8 (POOA[3])	Log Reduction S. aureus	Log Reduction E. coli
1	25 ppm	0	0	0, 0.2	0.5, 0.5
2	50 ppm	0	0	1.6, 1.4	1.9, 2.5
3	0	25 ppm	0	0,0	0.4,0.4
4	0	50 ppm	0	0.1, 0.1	1.4, 1.2
5	0	0	5 ppm	>6,6.0	1.6, 1.6
6	25 ppm	25 ppm	0	1.2, 1.2	2.7, 2.9
7	25 ppm	50 ppm	0	2.1, 1.9	>7, >7
8	0	25 ppm	5 ppm	>6, >6	5.0, >7
9	0	50 ppm	5 ppm	>6, >6	>7, >7
10	25 ppm	0	5 ppm	>6	>7

1 POAA = Peroxyacetic Acid, a C_2 acid

2 POGA = Peroxyglutaric Acid, a C_5 acid

3 POOA = Peroxyoctanoic Acid, a C_8 acid

The above data clearly shows a much greater than additive antimicrobial activity (synergism) when the peroxyglutaric (C_5) acid was combined with peroxyoctanoic (C_8) acid (Samples 8 and 9). A similar but weaker effect was obtained when peroxyacetic (C_2) acid was combined with peroxyglutaric acid (Samples 6 and 7).

It should be noted that S. aureus is very sensitive to peroxyoctanoic acid, thus it is difficult to use this organism to demonstrate a synergism between peroxyoctanoic acid and other peroxyacids. However, E. coli is not particularly sensitive to any of the above single peroxyacids at the concentrations tested (see Samples 1-5), but combinations of peroxyglutaric acid with either peroxyacetic acid or peroxyoctanoic acid were surprisingly active. The combination of peroxyglutaric acid with peroxyoctanoic acid was particularly effective, and this combination displays a marked synergism (especially note the data for E. coli for Samples 8 and 9 and compare with the additive effects of Samples 3 or 4 with Sample 5). Thus, a combination of these two peroxyacids (C_5 and C_8) displays surprisingly effective bacterial kill against these representative gram positive and gram negative microorganisms at concentrations that provide real economic and safety benefits.

Example 16

Two formulas were prepared with the following ingredients as listed in Table XII.

TABLE XII

Ingredient	Formula 1 (wt-%)	Formula 2 (wt-%)
H_2O_2 (35%)	89	81
Dequest 2010	1	1
Glutaric Acid	10	10
Octanoic Acid	--	3
n-Octane Sulfonate	--	5
	100	100

Each of the above formulas was allowed to stand at room temperature and equilibriate for seven days and was then titrated for total peroxyacid (calculated as peroxyglutaric acid). Formula 1 contained 7.49% peroxyglutaric acid, while Formula 2 contained 7.78% peroxyacids (calculated as peroxyglutaric acid but really a mixture of POGA and POOA).

The bacterial kill properties of the above two formulas were examined using E. coli as the test organism at room temperature in deionized water at 50 ppm total peroxyacid (as determined by titration of each formula, followed by appropriate dilution). The results are summarized in Table XIII below.

TABLE XIII

Bacterial Kill, E. coli, at 50 ppm Peroxyacid

	Log Reduction pH			
	2.2	4.0	6.0	8.0
Formula 1	4.2	5.3	0.7	0.3
Formula 2	>6.9	>7.2	>7.2	3.2

Thus, 50 ppm of the peroxyacids in Formula 2 has a much more effective kill than 50 ppm of peroxyglutaric acid alone in Formula 1.

The solubilizer present in Formula 2 does not contribute significantly to bacterial kill. Thus, we have shown a simple way of enhancing the kill properties of peroxyglutaric acid. We merely formulate a product that contains hydrogen peroxide, glutaric acid, an appropriate fatty acid, a stabilizer and a solubilizer (for the fatty acid). On standing, this mixture will form an equilibrium mixture of peroxyacids. Mixtures of appropriate peroxyacids will be synergistic and effective at low concentrations. Glutaric acid has a very low odor, and monocarboxylic acids of chain length of C_8 or greater, especially at these lower concentrations, are also of low odor. Thus, we can readily formulate synergistic compositions that possess acceptably low odor even in the concentrated formula, but especially at use dilutions.

Example 17

A mixture of short chain fatty acids commercially available from Emery Corporation under the designation "EMERY 658" was employed in producing a sanitizing concentrate composition of the present invention. The "EMERY 658" acid is a mixture of caprylic acid (C_8) and capric acid (C_{10}). The perfatty acids were prepared by the method of Parker, et al., J. Amer. Chem. Soc., 77, 4037 (1955) which is incorporated by reference. The perfatty acid component (also containing 34% acetic acid and 10% hydrogen peroxide) was combined with a pre-made solution of 10.42% peracetic acid, a separate amount of acetic acid, water, and an n-octanesulfonate hydrotrope coupler (NAS 8D). The final composition of this Example was as listed in Table XIV.

Example 18

A second composition of the present invention was prepared as described in Example 17, except that caprylic

acid (C_8) and capric acid (C_{10}) replaced some of the perfatty acid of Example 17. The concentration of peracetic acid was 5% while the concentration of perfatty acids was reduced to 1.5% (see Table XIV).

Example 19

The composition of Example 19 was prepared according to the procedure of Example 17, except that no peracetic acid or hydrogen peroxide was added to the composition. The acetic acid component was increased to 39 wt-% and the composition contained 5% perfatty acid (see Table XIV). Also, a chelating agent (Dequest 2010) was added to the composition.

Example 20

The composition of Example 20 was prepared the same as Example 19 except that caprylic acid and capric acid were added to the composition in addition to the percaprylic and percapric acid of Example 19. The composition contained 3.5% fatty acid and 1.5% perfatty acid (see Table XIV).

Example 21

Example 21 was prepared with only peracetic acid, acetic acid, hydrogen peroxide, and water. No perfatty acids or fatty acids were added to the composition of Example 21. The concentration of total peracid was about 5% and the acetic acid concentration was about 39% (see Table XIV).

Example 22

Example 22 was prepared the same as Example 20 except that no peracids were employed, only a mixture of fatty acids and acetic acid was used, along with water, NAS 8D, and Dequest 2010. The composition contained 5% fatty acid (see Table XIV).

TABLE XIV

Ingredient	Wt-% of Ingredients					
	Ex.17	Ex.18	Ex.19	Ex.20	Ex.21	Ex.22
Peracetic Acid (10.42% solution, 34% acetic acid, 10% H_2O_2)	50	50	--	--	50	--
Acetic Acid	22	22	39	39	22	39
Percaprylic Acid (C_8)	3.75	1.125	3.75	1.125	--	--
Percapric Acid (C_{10})	1.25	0.375	1.25	0.375	--	--
Caprylic Acid (C_8)	--	2.625	--	2.625	--	3.75
Capric Acid (C_{10})	--	0.875	--	0.875	--	1.25
NAS 8D	10	10	10	10	--	10
Water	13	13	45	45	28	45
Dequest 2010	--	--	1	1	--	1

Antimicrobial Efficacy of Examples 17-22

The compositions prepared according to Examples 17-22 were tested for their antimicrobial efficacy using the testing procedure of the standard A.O.A.C. sanitizing test. All of the samples tested of Examples 17-22 were made about 1 hour prior to testing. The bacteria used in the test procedure were S. aureus and E. coli. Distilled water was used to dilute the concentrate compositions of Examples 17-22 and the composition was employed at room temperature. The following neutralizers were employed in the test: 0.1% thiosulfate, peptone, 0.5% K_2HPO_4, 0.025% catalase for peracetic acid; chambers for fatty acid; 0.1% thiosulfate,

peptone, 0.025% catalase for peracetic acid/fatty acid (perfatty acid).

The antimicrobial activity of Examples 17-22 are summarized in Table XV. Examples 17 and 18 were tested using four samples (a,b,c,d) and Examples 19-22 were tested using two samples (a,b). As can be seen in Table XV, Examples 17-20 exhibited excellent kill (> log 6) of both S. aureus and E. coli at 50 ppm of peracid. Examples 21 and 22 (containing no perfatty acids) exhibited little or no activity. More specifically, Example 17 was tested at 1,000 and 500 ppm total product (50 and 25 ppm of both peroxyacetic acid and perfatty acid). At these low concentrations, the peracid combination gave a 6-7 log reduction in the bacterial count. Example 18 was tested at 1,000 and 500 ppm total product, and also had a 6-7 log reduction in the bacterial count. At the 500 ppm product concentration the product corresponds to 25 ppm of peroxyacetic acid and 7.5 ppm of perfatty acids. Example 19, at 1,000 ppm of total product (50 ppm of perfatty acid), completely killed all bacteria (greater than 7 log reduction). Example 20 also resulted in a complete kill using 1,000 ppm of total product (15 ppm perfatty acid). Example 21 contained no perfatty acid (only 50 ppm of peroxyacetic acid) and showed no activity against S. aureus and poor activity against E. coli. This is due to the fact that peroxyacetic acid is generally not effective at this level, and is generally used at concentrations greater than 100 ppm. Example 22, containing 5% fatty acid (30 ppm) and no perfatty acid at 1,000 ppm total product showed no activity toward either organism.

TABLE XV

Ex.	Sample	Test Product Concentration (ppm)	POAA[1]/POFA[2]/FA[3] Concentration (ppm)	pH	Log_{10} Kill S. aureus	Log_{10} Kill E. coli
17	a	1000	50/50/0	3.5	6.13	>7.30
	b	1000	50/50/0	3.5	6.52	7.30
	c	500	25/25/0	3.68	6.63	7.00
	d	500	25/25/0	3.68	6.78	7.30
18	a	1000	50/15/35	3.52	7.18	7.30
	b	1000	50/15/35	3.52	6.63	6.90
	c	500	25/7.5/17.5	3.68	6.70	6.76
	d	500	25/7.5/17.5	3.68	7.18	7.00
19	a	1000	0/50/0	3.5	>7.18	>7.30
	b	1000	0/50/0	3.5	>7.18	>7.30
20	a	1000	0/15/35	3.5	>7.18	>7.30
	b	1000	0/15/35	3.5	>7.18	>7.30
21	a	1000	50/0/0	3.49	NMA[4]	3.48
	b	1000	50/0/0	3.49	NMA	3.80
22	a	1000	0/0/30	3.46	NMA	NMA
	b	1000	0/0/30	3.46	NMA	NMA

1 - POAA = Peroxyacetic Acid
2 - POFA = Peroxyfatty Acid
3 - FA = Fatty Acid
4 - NMA = No measurable activity

Examples 23-26

Examples 23-26 were prepared by substantially the same procedure as the previous Examples, except that hydrogen peroxide (H_2O_2) was mixed with acetic acid and C_{8-10} fatty acids (Emery 658) to make the peracids of the composition. Table XVI summarizes the components and amounts of the various compositions of Examples 23-26 which were made.

TABLE XVI

Peracid Test Formulations

Ingredient	Ex. 23	Ex. 24	Ex. 25	Ex. 26
Acetic Acid	44	39	34	49
H_2O_2 (35%)	40	40	40	40
Dequest 2010	1	1	1	1
NAS 8D	10	10	10	10
Emery 658	5	10	15	--

Peracid Stability, Cidal Activity of Examples 23-26

Each of Examples 23-26 were tested for peracid stability and cidal activity using the A.O.A.C. sanitizing test against S. aureus and E. coli at room temperature with the formulations diluted in distilled water. Tables XVII-XX show the cidal activity of each formulation. Generally all of the formulations reached maximum peracid formation within about 12 days. All of the formulations obtained about 12.5% peracid except Example 25 (15% fatty acid) which obtained about 11.5% peracid.

Table XVII summarizes the cidal activity of Example 23 in which the composition was measured for cidal activity on the first day up to day 33. At 250 ppm of total product, there were about 4-5 ppm of perfatty acid and about 20 ppm of peracetic acid as determined by carbon 13 NMR

spectroscopy of the concentrate. The results are summarized in Table XVII.

TABLE XVII

Peracid Stability, Cidal Activity of Example 23

Day	Peracid Percent	Test[a] Concentration	Test pH	Ave. Log Reduction S. aureus	Ave. Log Reduction E. coli
1	4.28	250 ppm	3.92	6.28	NMA[b]
6	11.00	250 ppm	3.91	>7.38	>7.18
8	11.08	250 ppm	3.86	>7.11	>7.12
12	12.43	250 ppm	3.83	>7.18	6.96
15	12.74	250 ppm	3.88	6.95	--
33	10.18	250 ppm	3.83	5.18	6.34

[a] ppm total product

[b] No measurable activity

The cidal activity of Example 24 is summarized in Table XVIII below. The peracetic acid concentration at 250 ppm of product was about 20-21 ppm and the concentration of perfatty acid was about 11 ppm. The concentration of peracetic acid at 50 ppm of product was about 4 ppm and the concentration of perfatty acid was about 2 ppm.

TABLE XVIII

Peracid Stability, Cidal Activity of Example 24

Day	Peracid Percent	Test[a] Concentration	Test pH	Ave. Log Reduction S. aureus	Ave. Log Reduction E. coli
1	4.88	250 ppm	3.95	>7.60	NMA[b]
6	10.62	250 ppm	3.92	>7.38	>7.18
8	11.61	250 ppm	3.98	>7.11	>7.12
12	12.47	250 ppm	3.91	>7.18	>7.23
15	12.00	250 ppm	3.95	6.95	--
		120 ppm	4.18	>7.13	--
		50 ppm	4.41	6.39	--
33	10.49	250 ppm	3.85	5.20	6.22

[a] ppm total product

[b] No measurable activity

The cidal activity of Example 25 is summarized in Table XIX below. At 250 ppm of product the peracetic acid concentration was about 19 ppm and the perfatty acid concentration was about 14 ppm.

TABLE XIX

Peracid Stability,
Cidal Activity of Example 25

Day	Peracid Percent	Test[a] Concentration	Test pH	Ave. Log Reduction S. aureus	Ave. Log Reduction E. coli
1	4.84	250 ppm	3.90	>7.60	NMA[b] 4.04
6	9.81	250 ppm	3.96	>7.38	>7.18
8	10.99	250 ppm	3.96	>7.11	>7.12
12	11.47	250 ppm	3.94	>7.18	>7.23
15	11.48	250 ppm	3.96	6.83	--
33	10.49	250 ppm	3.95	5.25	6.53

[a] ppm total product

[b] No measurable activity

The cidal activity of Example 26 is summarized in Table XX below. At 250 ppm of product there was about 27 ppm of peracetic acid. At 1000 ppm of product there was about 108 ppm of peracetic acid. No fatty acid was employed in the composition of Example 26.

TABLE XX

Cidal Activity of Example 26

Day	Peracid Percent	Test[a] Concentration	Test pH	Ave. Log Reduction S. aureus	E. coli
5	10.95	250 ppm	3.90	NMA[b]	NMA
7	12.03	1000 ppm	3.50	4.60	>7.12
11	12.44	1000 ppm	3.49	6.38	6.64
14	12.53	1000 ppm	3.50	4.17	--
32	10.77	1000 ppm	3.45	4.77	6.44

[a] ppm total product

[b] No measurable activity

When comparing the formulations containing fatty acid (Tables XVII-XIX), poor activity was measured against E. coli one day after being formulated. Since the total peracid values were low, more fatty acid was present and gram negative bacteria tend to be less sensitive than gram positive bacteria to the C_8-C_{10} fatty acids. However, as more peracid developed over the days indicated, increased cidal activity against E. coli was observed. Table XX indicates that to obtain acceptable activity (greater than or equal to 5 log reduction) using only peracetic acid, the peracetic acid must be tested over 100 ppm active. Secondly, this oxidizing compound is more effective against E. coli than S. aureus.

Generally all the formulations containing fatty acid remain stable after about 1 month. This was confirmed by repeated testing over time at 250 ppm total product for each formulation in which greater than 5 log reductions were measured against S. aureus and E. coli.

Examples 27-32

The cidal activity of a two-component system containing both peracetic acid and fatty acid was investigated using the A.O.A.C. sanitizing test. Table XXI shows the product formulations examined. The test samples include controls showing cidal activity of NAS 8D as well as fatty acid kill against S. aureus. All the samples were tested in distilled water.

TABLE XXI

	Wt-% Ingredient					
Ingredient	Ex.27	Ex.28	Ex.29	Ex.30	Ex.31	Ex.32
Base 1[(a)]	80	80	80	80	--	--
Base 2[(b)]	--	--	--	--	80	80
NAS 8D	10	--	10	10	10	10
Octanoic Acid	--	--	10	--	--	10
Emery 658	--	--	--	10	10	--
H_2O	10	20	--	--	--	--

(a) H_2O_2, 35%; acetic acid, 35%; Dequest 2010, 1%; H_3PO_4 (85%), 29%.

(b) Acetic acid, 35%; Dequest 2010, 1%; H_3PO_4 (85%), 29%; H_2O, 35%.

Table XXII shows the activity measurement of each of Examples 27-32 at various test concentrations. When testing the peracetic acid formulation of Examples 27 and 28 (having no fatty acid), biocidal activity occurred only at 100 ppm or greater. Cidal activity (greater than 4 log reduction) was measured at a minimal concentration of 10 ppm peracid with fatty acid in the system (Example 29). At 10 ppm peracid, the composition containing Emery 658 (Example 30) had better activity than the system containing only C_8 (octanoic) fatty acid (Example 29). In the fatty acid controls having no oxidant (Examples 31 and 32), the

Emery 658 had more cidal activity than the C_8 fatty acid. At total product test concentrations equivalent to 10 or 25 ppm peracid, the fatty acid in the system of Example 31 did not have significant cidal activity. Example 32 did not have significant cidal activity at any test concentration.

TABLE XXII

Peracid Cidal Activity Against S. aureus

Example	Peracid (%)	Concentration (ppm Peracid)	Test pH	Log[a] Reduction
27	7.02	50	2.79	NMA[b]
		100	2.54	5.45
		150	2.41	>7.70
28	6.25	50	2.76	NMA
		100	2.52	4.51
		150	2.40	5.84
29	9.32	10	3.52	4.22
		25	3.16	>7.70
		50	2.90	>7.70
30	9.73	10	3.50	6.82
		25	3.19	7.55
		50	2.88	>7.70
31	--	--[c]	3.53	0.70
		--[c-1]	3.18	1.04
		--[c-2]	2.88	4.07
32	--	--[d]	3.51	0.93
		--[d-1]	--	0.66
		--[d-2]	--	0.97

(a) Average of duplicate testing.

(b) No measurable activity.

(c) Same total product concentration as Example 30 @10 ppm peracid (about 100 ppm product).

(c-1) Same total product concentration as Example 30 @25 ppm peracid (about 250 ppm product).

(c-2) Same total product concentration as Example 30 @50 ppm peracid (about 500 ppm product).

(d) Same total product concentration as Example 29 @10 ppm peracid (about 100 ppm product).

(d-1) Same total product concentration as Example 29 @25 ppm peracid (about 250 ppm product).

(d-2) Same total product concentration as Example 29 @50 ppm peracid (about 500 ppm product).

The cidal activity of a peracetic acid/fatty acid system was measured comparing freshly made formulations to month-old formulations of Examples 30 and 31. These formulations are shown in Table XXIII which compares the titration values of month-old formulations to the same freshly prepared. Table XXIV shows the cidal activity of month-old and fresh formulations of Examples 29 and 30.

TABLE XXIII

Peracid Titration Values

	Ex. 29	Ex. 30	Ex. 29	Ex. 30
Date formulated	Month-Old	Month-Old	Fresh	Fresh
% H_2O_2	2.15	2.07	1.99	1.99
% Peracid	5.37	5.35	4.85	4.86
% Total O_2	2.14	2.10	1.96	1.96

TABLE XXIV

Peracid Cidal Activity Against S. aureus

Example	Peracid (%)	Test Concentration (ppm Peracid)	Test pH	Log[a] Reduction
29	5.37	10	3.46	NMA[b]
(Month-Old)		25	3.07	>7.48
29	4.85	10	3.34	5.07
(Fresh)		25	2.97	7.30
30	5.35	10	3.52	5.29
(Month-Old)		25	3.04	7.24
30	4.86	10	3.42	NMA[c]/
(Fresh)		25	2.99	7.48

(a) Average of duplicate testing.

(b) No measurable activity (3.68 log reduction).

(c) Duplicate testing in which only one sample exhibited cidal activity.

As can be seen from Table XXIV, cidal activity in the peracetic acid/fatty acid system occurs at test concentrations as low as 10 or 25 ppm peracid. Mixed results occurred at 10 ppm peracid between the month-old and fresh formulations of Examples 29 and 30, however, increasing the concentration to 25 ppm resulted in a uniform kill activity (>7 log reduction).

An additional test was run to determine how quickly compounds exhibiting cidal activity are formed upon adding

fatty acid to a peracetic acid system. Examples 27, 30 and 31 were tested. Examples 27 and 30 were formulated the day before testing and were day-old samples. Another test sample of Example 30 was formulated immediately prior to testing. Example 31 containing Base 2 (no H_2O_2) was used to show cidal activity from the fatty acid at low test concentrations. Table XXV shows the cidal activity of each Example in distilled water against S. aureus.

TABLE XXV

Cidal Activity Against S. aureus

Example	Age	ppm Peracid	Test pH	Log[a] Reduction
27	1 day	50	2.94	NMA[b]
		100	2.71	6.60
28	1 day	10	3.68	7.02
		25	3.35	>7.20
30	fresh	10	3.76	NMA
		25	3.32	NMA
31	22 days	__[c]	3.74	NMA
		__[d]	__	NMA

(a) Average of duplicate testing.

(b) No measurable activity.

(c) Equivalent total product concentration as Example 30 (day old) @ 10 ppm peracid.

(d) Equivalent total product concentration as Example 30 (day old) @ 25 ppm peracid.

The data from Table XXV suggests that the formation of compounds containing cidal activity when adding fatty acid to a peracetic acid system is not immediate, but does occur within a day. The formation of compounds exhibiting cidal activity occurred within a day after adding fatty acid to the peracetic acid system as in Example 30 with cidal activity occurring at a concentration as low as 10 ppm peracid. Thus, the cidal activity is not due to the mere combination of fatty acid and peroxyacetic acid, but the fatty acid must be converted to the perfatty acid before substantially enhanced cidal activity occurs.

The foregoing discussion and Examples are illustrative of the invention. However, since many embodiments of the invention can be made without departing from the spirit and scope of the invention, the invention resides in the claims hereinafter appended.

WE CLAIM:

1. A peroxyacid antimicrobial concentrate composition comprising:

(a) an effective biocidal amount of a C_5 peroxyacid; and

(b) an effective biocidal amount of a peroxyacid selected from the group consisting of an aliphatic C_6-C_{18} peroxyacid, a C_1-C_4 peroxyacid, and mixtures thereof;

wherein the concentrate composition is capable of being diluted with a major proportion of water to form an antimicrobial use solution that can achieve a 5 log reduction in a microbial population at a pH in the range of about 2 to 8.

2. The concentrate composition of claim 1 which comprises about 1 to 25 wt-% of said C_5 peroxyacid.

3. The concentrate composition of claim 1 wherein said C_5 peroxyacid is peroxyglutaric acid.

4. The concentrate composition of claim 1 which comprises about 0.01 to 20 wt-% of said peroxyacid of (b).

5. The concentrate composition of claim 1 wherein said C_1-C_4 peroxyacid is selected from the group consisting of peroxyacetic acid, peroxypropionic acid, peroxysuccinic acid, peroxyglycolic acid, peroxylactic acid and mixtures thereof.

6. The concentrate composition of claim 1 wherein said C_6-C_{18} peroxyacid is selected from the group consisting of an aliphatic monoperoxy carboxylic acid or a diperoxydicarboxylic acid.

7. The concentrate composition of claim 6 wherein said C_6-C_{18} peroxyacid is selected from the group consisting of peroxyoctanoic acid, peroxydecanoic acid, monoperoxy- or diperoxyadipic acid, monoperoxy- or diperoxysebacic acid, and mixtures thereof.

8. The concentrate composition of claim 1 wherein the weight ratio of said C_5 peroxyacid to said peroxyacid of (b) is about 20:1 to 1:10 and the microbial population is reduced in less than 120 seconds.

9. The concentrate composition of claim 1 further comprising an effective amount of a hydrotrope coupling agent capable of solubilizing said C_6-C_{18} peroxyacid in the concentrate and when the concentrate is diluted with water.

10. The concentrate composition of claim 9 wherein said concentrate comprises about 0.1 to 30 wt-% of said hydrotrope coupling agent.

11. The concentrate composition of claim 10 wherein said hydrotrope is selected from the group consisting of n-octanesulfonate, a xylene sulfonate, a naphthalene sulfonate, and mixtures thereof.

12. The concentrate composition of claim 1 further comprising a carboxylic acid selected from the group consisting of a C_5 carboxylic acid, a C_1-C_4 carboxylic acid, an aliphatic C_6-C_{18} carboxylic acid, and mixtures thereof.

13. The concentrate composition of claim 12 wherein said C_5 carboxylic acid is glutaric acid, and said C_1-C_4 carboxylic acid is selected from the group consisting of acetic acid, propionic acid, succinic acid, glycolic acid, lactic acid and mixtures thereof.

14. The concentrate composition of claim 12 wherein said C_6-C_{18} carboxylic acid is selected from the group consisting of octanoic acid, decanoic acid, adipic acid, sebacic acid, and mixtures thereof.

15. The concentrate composition of claim 1 further comprising hydrogen peroxide.

16. The concentrate composition of claim 15 wherein said concentrate comprises about 1 to 50 wt-% of said hydrogen peroxide.

17. The concentrate composition of claim 1 wherein said composition can form a use solution having a pH of about 3 to 7 and the microbial population is reduced in less than 30 seconds.

18. A peroxyacid antimicrobial concentrate composition comprising:

(a) about 0.01 to 25 wt-% of a C_5 peroxyacid;

(b) about 0.01 to 10 wt-% of a peroxyacid of the structure R_1-CO_3H, wherein R_1 comprises an aliphatic hydrocarbon chain having about 5 to 17 carbon atoms;

(c) about 0.1 to 30 wt-% of a hydrotrope coupling agent capable of solubilizing said peroxyacid of (b) in the concentrate and when the concentrate is diluted with water; and

(d) about 1 to 50 wt-% of hydrogen peroxide;

wherein the concentrate composition is capable of being diluted with a major proportion of water to form an antimicrobial sanitizing use solution that can achieve a 5 log reduction in a microbial population at a pH in the range of about 3 to 7.

19. The concentrate composition of claim 18 wherein said C_5 peroxyacid is peroxyglutaric acid.

20. The concentrate composition of claim 18 wherein said peroxyacid of (b) is a peroxyfatty acid having about 8 to 12 carbon atoms per molecule.

21. The concentrate composition of claim 20 wherein said peroxyfatty acid is peroxyoctanoic acid, peroxydecanoic acid, or mixtures thereof.

22. The concentrate composition of claim 20 wherein the weight ratio of said C_5 peroxyacid to said peroxyfatty acid is about 20:1 to 2:1.

23. The concentrate composition of claim 18 wherein said hydrotrope comprises n-octanesulfonate.

24. The concentrate composition of claim 20 further comprising about 5 to 50 wt-% of a carboxylic acid selected

from the group consisting of a fatty acid, a C_5 carboxylic acid, and mixtures thereof.

25. The concentrate composition of claim 24 wherein said C_5 carboxylic acid is glutaric acid.

26. The concentrate composition of claim 24 wherein said fatty acid is octanoic acid, decanoic acid, or mixtures thereof.

27. An aqueous peroxyacid antimicrobial composition comprising:

(a) at least about 10 parts per million (ppm) of a C_5 peroxyacid; and

(b) at least about 1 ppm of a peroxyacid selected from the group consisting of a C_6-C_{18} peroxyacid, a C_1-C_4 peroxyacid, and mixtures thereof;

wherein the aqueous composition has a pH in the range of about 2 to 8.

28. The aqueous composition of claim 27 wherein said C_5 peroxyacid is peroxyglutaric acid.

29. The aqueous composition of claim 27 wherein said C_1-C_4 peroxyacid is selected from the group consisting of peroxyacetic acid, peroxypropionic acid, peroxysuccinic acid, peroxyglycolic acid, peroxylactic acid and mixtures thereof.

30. The aqueous composition of claim 27 wherein said C_6-C_{18} peroxyacid is an aliphatic peroxyfatty acid, or an aliphatic monoperoxy- or diperoxydicarboxylic acid.

31. The aqueous composition of claim 27 wherein said C_6-C_{18} peroxyacid is selected from the group consisting of peroxyoctanoic acid, peroxydecanoic acid, monoperoxy- or diperoxyadipic acid, monoperoxy- or diperoxysebacic acid, and mixtures thereof.

32. The aqueous composition of claim 27 further comprising at least about 1 ppm of a hydrotrope coupling agent.

33. The aqueous composition of claim 27 wherein the weight ratio of said C_5 peroxyacid to said peroxyacid of (b) is about 20:1 to 1:10.

34. The aqueous composition of claim 27 further comprising at least about 10 ppm of a carboxylic acid selected from the group consisting of a C_5 carboxylic acid, a C_1-C_4 carboxylic acid, a C_6-C_{18} carboxylic acid, and mixtures thereof.

35. The aqueous composition of claim 34 wherein said C_5 carboxylic acid is glutaric acid, and said C_1-C_4 carboxylic acid is selected from the group consisting of acetic acid, propionic acid, succinic acid, glycolic acid, lactic acid and mixtures thereof.

36. The aqueous composition of claim 34 wherein said C_6-C_{18} carboxylic acid is selected from the group consisting of octanoic acid, decanoic acid, adipic acid, sebacic acid, and mixtures thereof.

37. The aqueous composition of claim 27 further comprising at least about 1 ppm of hydrogen peroxide.

38. An aqueous peroxyacid antimicrobial sanitizing composition comprising:

(a) about 10 to 75 parts per million (ppm) of a C_5 peroxyacid;

(b) about 1 to 25 ppm of a peroxyacid of the structure R_1-CO_3H wherein R_1 comprises aan aliphatic hydrocarbon chain having about 5 to 17 carbon atoms;

(c) about 1 to 200 ppm of a hydrotrope coupling agent; and

(d) about 2 to 200 ppm of hydrogen peroxide;

wherein the aqueous composition has a pH in the range of about 3 to 7.

39. The aqueous composition of claim 38 wherein said C_5 peroxyacid is peroxyglutaric acid.

40. The concentrate composition of claim 38 wherein said peroxyacid of (b) is a peroxyfatty acid having about 8 to 12 carbon atoms per molecule.

41. The aqueous composition of claim 40 wherein said peroxyfatty acid is peroxyoctanoic acid, peroxydecanoic acid, or mixtures thereof.

42. The aqueous composition of claim 38 wherein said hydrotrope comprises n-octanesulfonate.

43. The aqueous composition of claim 40 further comprising about 10 to 800 ppm of a carboxylic acid selected from the group consisting of a fatty acid, a C_5 carboxylic acid, and mixtures thereof.

44. The aqueous composition of claim 43 wherein said C_5 carboxylic acid is glutaric acid.

45. The aqueous composition of claim 43 wherein said fatty acid is octanoic acid, decanoic acid, or mixtures thereof.

46. A method of sanitizing substantially fixed in-place process facilities comprising the steps of:

(a) introducing into the process facilities the composition of claim 27 at a temperature in the range of about 4°C to 60°C;

(b) circulating the composition through the process facilities for a time sufficient to sanitize the process facilities; and

(c) draining the composition from the process facilities.

47. The method of claim 46 wherein said composition is circulated through the process facilities for about 30 minutes or less.

48. The method of claim 46 wherein after said draining of said composition from the process facilities, the process facilities are rinsed with potable water.

49. The method of claim 46 wherein the process facilities comprise a milk line dairy.

50. The method of claim 46 wherein the process facilities comprise a continuous brewing system.

51. The method of claim 46 wherein the process facilities comprise a pumpable food system or beverage processing line.

52. The method of claim 46 wherein the population is reduced in less than 120 seconds.

53. The method of claim 46 wherein the population is reduced in less than 60 seconds.

54. A method of sanitizing or disinfecting a solid surface or liquid media by bringing the surface or media into contact with the composition of claim 27 at a temperature in the range of about 4°C to 60°C for an effective period of time sufficient to sanitize or disinfect the solid surface or liquid media, wherein the population is reduced in less than 120 seconds.

55. A process for sanitizing, disinfecting or sterilizing a contaminated surface using a peroxyacid antimicrobial concentrate composition, comprising the steps of:

(a) diluting in an aqueous liquid said antimicrobial concentrate, thereby forming an aqueous antimicrobial solution, said antimicrobial concentrate comprising:

(i) about 1 to 25 wt-% of a C_5 peroxyacid; and

(ii) about 0.01 to 10 wt-% of a C_6-C_{18} peroxyacid;

wherein said aqueous antimicrobial solution has a pH of about 2 to 8; and

(b) contacting said aqueous antimicrobial solution with said contaminated surface for a period of time effective to sanitize, disinfect, or sterilize said surface.

56. The process of claim 55 wherein the population is reduced in less than 120 seconds.

57. The process of claim 55 wherein the population is reduced in less than 60 seconds.

58. The process of claim 55 wherein said antimicrobial concentrate further comprises about 0.1 to 30 wt-% of a hydrotrope coupling agent capable of solubilizing said C_6-C_{18} peroxyacid in the concentrate and when the concentrate is diluted with water.

59. The process of claim 55 wherein said C_5 peroxyacid is peroxyglutaric acid.

60. The process of claim 55 wherein said C_6-C_{18} peroxyacid is selected from the group consisting of peroxyoctanoic acid, peroxydecanoic acid, monoperoxy- or diperoxyadipic acid, monoperoxy- or diperoxysebacic acid, and mixtures thereof.

61. The process of claim 58 wherein said hydrotrope coupling agent is selected from the group consisting of n-octanesulfonate, a xylene sulfonate, a naphthalene sulfonate, and mixtures thereof.

62. The process of claim 55 wherein the contaminated surface is an inanimate solid surface contaminated by a biological fluid comprising blood, other hazardous body fluids, or mixtures thereof.

63. The process of claim 55 wherein the contaminated surface comprises the surface of food service, ware or equipment.

64. The process of claim 55 wherein the contaminated surface comprises the surface of a fabric.

65. The composition of claim 55 further comprising an effective amount of a chelating agent for binding polyvalent metal cations.

66. The composition of claim 65 wherein said chelating agent is 1-hydroxyethylidene-1,1-diphosphonic acid.

67. The composition of claim 18 further comprising a chelating agent for binding polyvalent metal cations.

68. The composition of claim 67 wherein said chelating agent is 1-hydroxyethylidene-1,1-diphosphonic acid.

69. The composition of claim 67 wherein said chelating agent is present in an amount of about 1 wt-% based on the concentrate composition.

70. The composition of claim 27 further comprising a chelating agent for binding polyvalent metal cations.

71. The composition of claim 70 wherein said chelating agent is 1-hydroxyethylidene-1,1-diphosphonic acid.

72. The composition of claim 38 further comprising a chelating agent for binding polyvalent metal cations.

73. The composition of claim 72 wherein said chelating agent is 1-hydroxyethylidene-1,1-diphosphonic acid.

74. A method of making a peroxyacid antimicrobial concentrate composition comprising the steps of:

(a) mixing a C_5 carboxylic acid with an aliphatic C_6-C_{18} carboxylic acid to form an organic acid mixture;

(b) adding hydrogen peroxide, a hydrotrope coupling agent, and a chelating agent to said organic acid mixture, thereby forming a concentrate mixture; and

(c) allowing said concentrate mixture to form an equilibrium mixture comprising an effective biocidal amount of a C_5 peroxyacid and an effective biocidal amount of an aliphatic C_6-C_{18} peroxyacid.

75. A peroxyacid antimicrobial concentrate composition made by the method of claim 74.

INTERNATIONAL SEARCH REPORT

Inte onal Application No
PCT/US 94/02134

A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 A01N37/16

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 5 A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO,A,93 01716 (ECOLAB INC.) 4 February 1993 see the whole document	1-75
X	US,A,4 129 517 (STERLING DRUG INC.) 12 December 1978 see the whole document	1-75
X	DE,A,35 43 500 (SCHÜLKE & MAYR GMBH) 11 June 1987 see claims 1 - 11 and examples.	27,28, 32-34,37
A	EP,A,0 461 700 (AKZO N.V.) 18 December 1991	1-75
P,A	EP,A,0 569 066 (UNILEVER N.V.) 10 November 1993	1-75

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

2

Date of the actual completion of the international search	Date of mailing of the international search report
16 August 1994	26. 08. 94

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Klaver, J

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 94/02134

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO-A-9301716	04-02-93	US-A- 5200189	06-04-93
		AU-A- 2176992	23-02-93
		CA-A- 2108177	24-01-93
		CN-A- 1068705	10-02-93
		EP-A- 0597877	25-05-94
		FI-A- 940231	17-03-94
		US-A- 5314687	24-05-94
US-A-4129517	12-12-78	DE-B- 2654164	22-12-77
		AT-B- 356289	25-04-80
		BE-A- 860976	16-03-78
		CA-A- 1081079	08-07-80
		CH-A- 635576	15-04-83
		FR-A,B 2371930	23-06-78
		GB-A- 1560525	06-02-80
		JP-A- 53081619	19-07-78
		LU-A- 78560	13-04-78
		NL-A- 7712569	01-06-78
		SE-B- 440848	26-08-85
		SE-A- 7712986	31-05-78
DE-A-3543500	11-06-87	NONE	
EP-A-0461700	18-12-91	NONE	
EP-A-0569066	10-11-93	AU-B- 3684293	21-10-93